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AN EXAMINATION OF
THE ADSORPTION CAPABILITIES
OF THE "MAGIC" BLACK ROCKS
OF THE LITTLE MISSOURI RIVER

Denise A. Leverett

Submitted in partial fulfillment of the
requirements for graduation with honors
from

THE CARL GOODSON HONORS PROGRAM

OUACHITA BAPTIST UNIVERSITY

1985

Approved by

Date

This reactivity between the adsorbent, the surface layer, and the adsorbate, the incoming atom or molecule, is a combination of two forces: coulombic, or electrostatic, attraction and the chemical reactivity of the surface groups. The physical nature of ionic interaction has long range effects and is responsible for the attraction of the adsorbent for the adsor-

Abstract

It has been seen that manganese oxides precipitate from aqueous solution as they pass downstream from cold water release reservoirs. This precipitation is visible in the form of black coatings on gravels in the river or stream bed. These oxide coatings not only cause the further oxidation and precipitation of manganese ions but also have the capacity for adsorbing trace metals from the system. The amount of metal adsorbed varies with the element. This study not only addresses the various elements which may be adsorbed but also the rates at which adsorption occurs and the factors which affect those rates, among these

Introduction

Adsorption may be defined as the attraction and attachment of atoms or molecules to other atoms or molecules present in the environment. This attachment may occur within layers of a substance; however, the mechanism of action most frequently discussed involves adsorption to the outermost layer.

The phenomenon of adsorption is the result of an imbalance in bonding of an atom or molecule. Constituents of the inner layers do not tend to display this process because valence bonding is complete. In the outer layer, the atoms or molecules possess unshared electrons or reactive groups which provide points of attachment.

This reactivity between the adsorbent, the surface layer, and the adsorbate, the incoming atom or molecule, is a combination of two forces: coulombic, or electrostatic, attraction and the chemical reactivity of the surface groups. The physical nature of ionic interaction has long range effects and is responsible for the attraction of the adsorbent for the adsorbate. Once the incoming atom or molecule is properly positioned, the energetically favorable chemical process imparts stability to the attachment.

In aquatic environments, adsorption is a driving force controlling the geochemistry of the system. This process has been shown to occur in various solid phases in the system, including hydrous oxides. Of particular interest among these hydrous oxides is manganese dioxide.

Manganese is present in the anoxic layer of lakes in muds and on other hypolimnetic solids as a reduced specie, the Mn^{+2} ion. As water is removed from cold water release reservoirs, this reduced manganese is released in the discharge. As the effluent makes its way downstream, the water becomes increasingly oxygenated, causing the Mn^{+2} ion to be oxidized to Mn^{+4} . This oxidation, according to Bricker (1965), may proceed by two pathways. The first possibility involves formation of an intermediate Mn_3O_4 while the second entails formation of an intermediate $MnOOH$. Both of these then react further to produce manganese dioxide, MnO_2 , which precipitates from solution.

This precipitation is aided by the presence of previously deposited MnO_2 , suggesting autocatalysis.

As precipitation occurs, it becomes visible on rocks and gravels as a black coating. Research conducted by Nix (1984) on the content of this black coating has shown that it is comprised primarily of manganese, iron, and aluminum. It also contains such trace metals as lead, nickel, zinc, copper, cobalt, cadmium and silver. Further experimentation has demonstrated that these seven trace metals may be removed from solution when gravels coated with manganese dioxide are present, as shown in Figure 1. Chromium was also introduced as a metallic specie but was not removed due to formation of the chromate ion.

Gray and Malati (1979 a, b) have shown that delta-manganese dioxide, which exists in soils and deep sea nodules, is not only capable of adsorbing alkaline-earth metals but also some heavy metal cations. Although their work on adsorption of heavy metals is supported by data gathered by Nix (1984), adsorption of calcium and magnesium is not demonstrated to an appreciable extent at the concentrations present in the riverine system being studied. This is not to say that adsorption is not occurring; rather, competitive adsorption may be favoring the removal of trace metals and their tighter binding than these alkaline-earths.

Work by Hasany and Qureshi (1981) confirms the ability of manganese dioxide to remove trace metals from aqueous solutions.

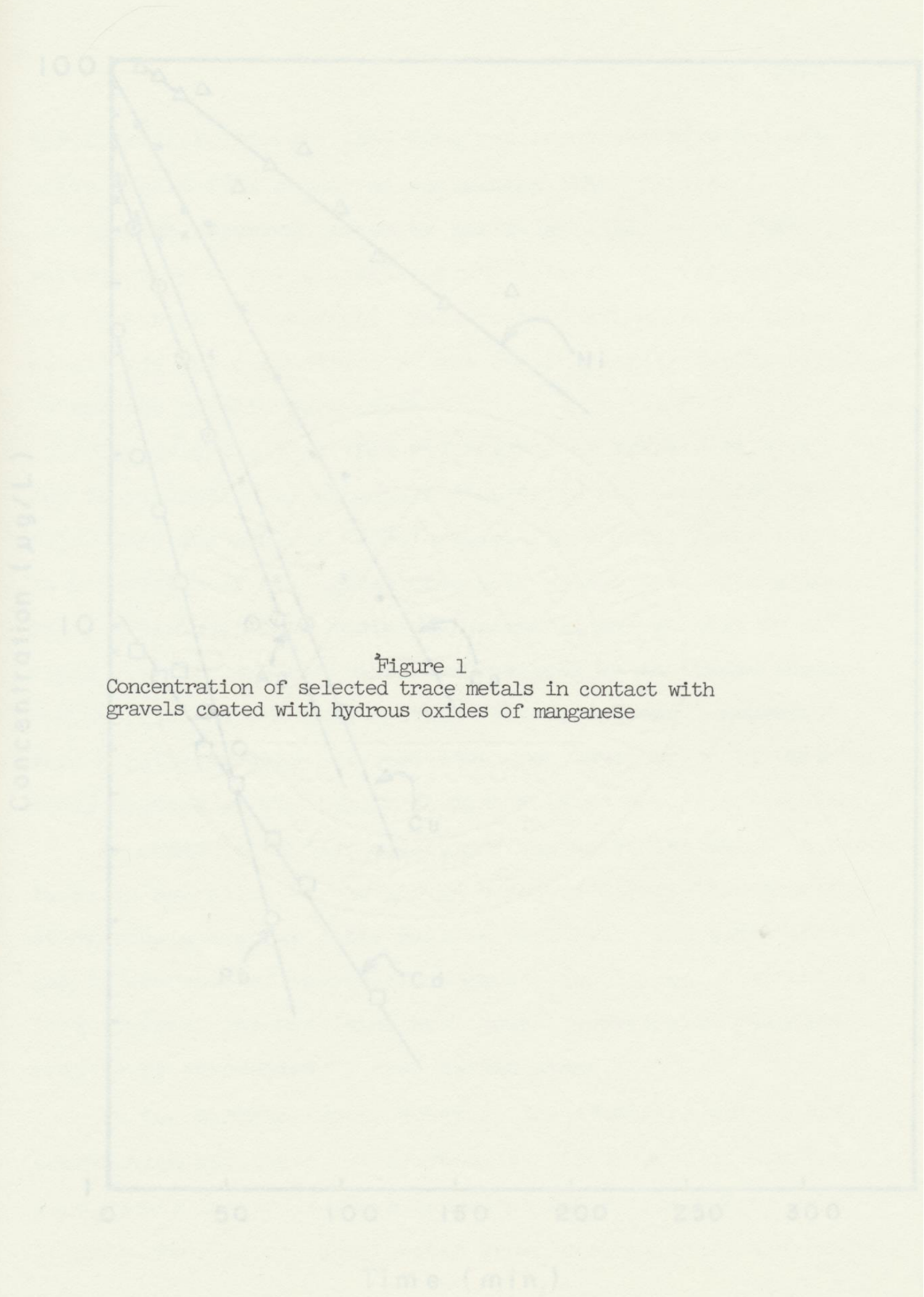
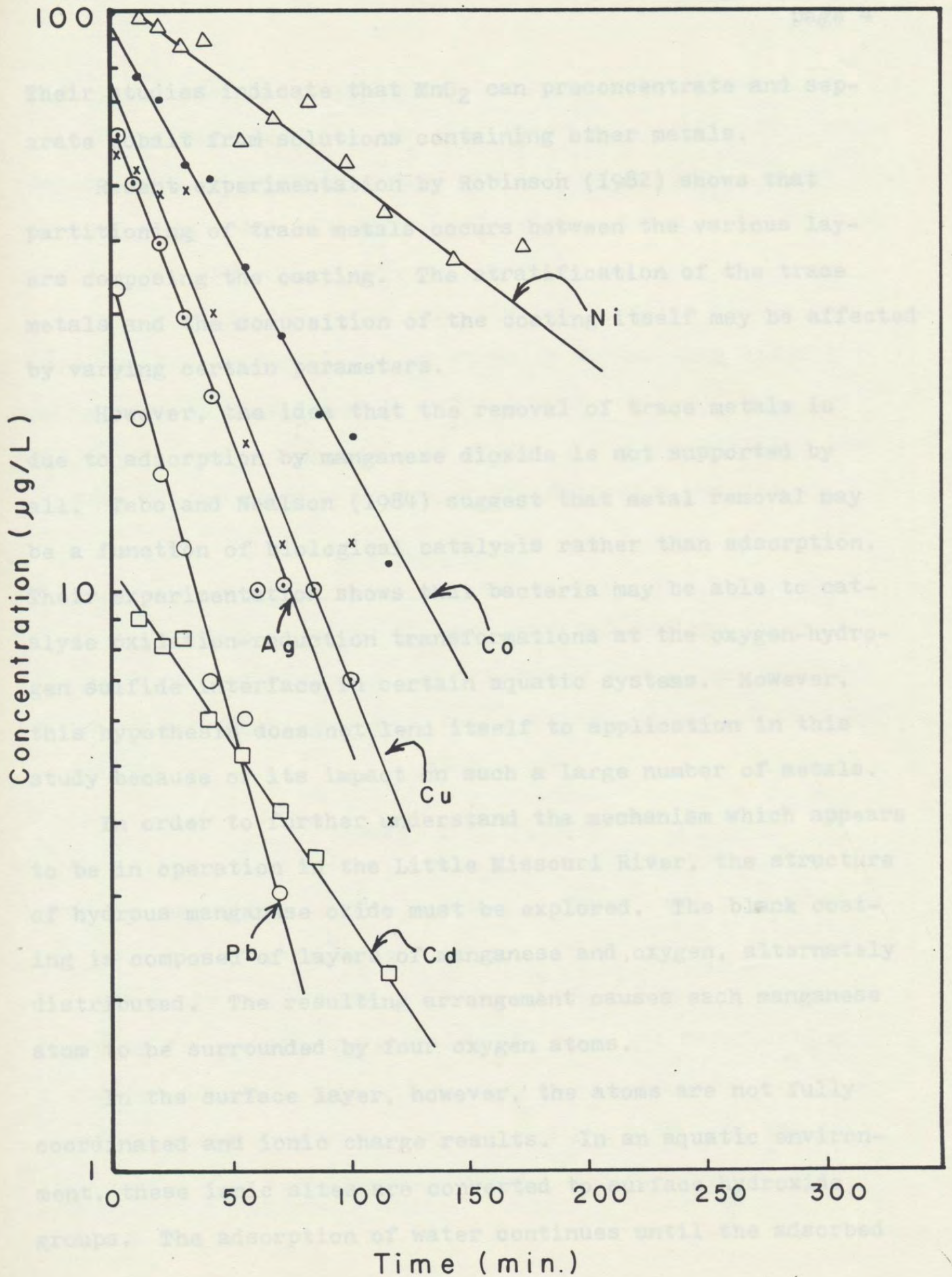


Figure 1
Concentration of selected trace metals in contact with
gravels coated with hydrous oxides of manganese



Their studies indicate that MnO_2 can preconcentrate and separate cobalt from solutions containing other metals.

Recent experimentation by Robinson (1982) shows that partitioning of trace metals occurs between the various layers composing the coating. The stratification of the trace metals and the composition of the coating itself may be affected by varying certain parameters.

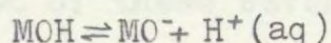
However, the idea that the removal of trace metals is due to adsorption by manganese dioxide is not supported by all. Tebo and Nealson (1984) suggest that metal removal may be a function of biological catalysis rather than adsorption. Their experimentation shows that bacteria may be able to catalyze oxidation-reduction transformations at the oxygen-hydrogen sulfide interface in certain aquatic systems. However, this hypothesis does not lend itself to application in this study because of its impact on such a large number of metals.

In order to further understand the mechanism which appears to be in operation in the Little Missouri River, the structure of hydrous manganese oxide must be explored. The black coating is composed of layers of manganese and oxygen, alternately distributed. The resulting arrangement causes each manganese atom to be surrounded by four oxygen atoms.

In the surface layer, however, the atoms are not fully coordinated and ionic charge results. In an aquatic environment, these ionic sites are converted to surface hydroxide groups. The adsorption of water continues until the adsorbed

liquid's properties approach those of the bulk liquid. As this layer thickens, the adsorbed water becomes highly dissociated, thus allowing increased mobility of protons. These protons may result either from the dissociation of water or the surface hydroxyl group.

As is indicated, this dissociation reaction at the surface is pH dependent. The pH at which the surface layer has no net charge is defined as point of zero charge (PZC), and its value varies from oxide to oxide. At a pH above PZC the surface of the coating undergoes the following reaction:



where M is representative of any metal which forms an oxide. The surface layer assumes a net negative charge and becomes a cation exchanger. At a pH below PZC the dissociation which occurs is



Thus the oxide has become an anion exchanger and possesses a net positive surface charge.

When the surface is neutral one would expect adsorption capacity to be lessened greatly. Without the far-reaching coulombic effects, adsorption would become dependent on the chemical reactivity of surface groups and such weak physical interactions as hydrogen, coordinate, and van der Waals bonding.

Under proper pH conditions, the surface of the hydrous manganese dioxide is capable of adsorbing a metallic cation from solution. If, however, the solution pH becomes too acidic by falling below the point of zero charge, desorption begins and the trace metal may be returned to solution. Although Gray and Malati (1979) have reported that adsorption is not strictly reversible, Hasany and Qureshi (1981) find that complete desorption of metal ions is possible with concentrated solutions of nitric or perchloric acid.

This study was undertaken in an attempt to explore the mechanism of adsorption of these seven metals. Furthermore, the investigation was also designed to examine factors which affect the rate of adsorption. Two which were considered were pH and ionic strength. Finally, research was conducted to determine the presence and amount of microbial catalysis in the aquatic system being studied.

Materials and methods

One liter of distilled water was placed in a two liter beaker containing a Pyrex dessicator platform and a stirring bar. Prewashed gravels obtained from the Little Missouri River below Lake Greeson were loaded onto the platform, and the solution was placed on a Corning PC-353 stirrer. The solution was then spiked with seven Fisher spectrophotometric grade trace metals. Cobalt, copper, lead, nickel, and zinc were added to a concentration of 100 ug/L. Cadmium and silver

were added to a concentration of 10 ug/L. These concentrations were used since they are representative of the levels at which these trace metals become environmentally significant. Upon equilibration, the pH of the solution was adjusted to a pre-determined level using dilute solutions of either dilute nitric or hydrochloric acid and dilute sodium hydroxide. All pH measurements were made using an Orion 231 pH meter.

After allowing sufficient time for mixing of the standards, sampling was begun. Samples were removed from each beaker using Millipore syringes and were placed in plastic vials. Subsequent acidification with concentrated nitric acid was carried out to maintain the metals in solution.

Sampling was conducted at half hour intervals for the first four to five hours. For the next four hours, hourly sampling was carried out. The remainder of the sample collection was taken at two hour intervals.

Samples were then analyzed for each trace metal using the Perkin Elmer 4000 atomic absorption spectrophotometer and the Perkin Elmer HGA 400 graphite furnace attachment.

Results and discussion

As was discussed previously, the adsorption of these seven trace metals is pH dependent and that dependence may be related to the point of zero charge. The PZC for manganese dioxide, as determined and reported by Morgan and Stumm (1964), is 2.8 ± 0.3 . At a pH below 2.8 adsorption of any of these cations would not occur due to electrostatic repulsion of a

positively charged surface. Thus, the trace metal would remain in solution.

However, as the pH of the system rises above the PZC, adsorption begins. The surface charge has become negative and the coulombic attraction of the negatively charged hydroxyl group for the positive metal ion is powerful enough to draw the cation through the diffuse double layer and down to the surface.

Also dependent on pH is the form of the cation which adsorbs to the black coating. At lower pH levels, the primary form of the adsorbate is the ionic form of the metal itself. As pH rises, hydrolysis of the metal increases, and adsorption may be demonstrated as a condensation reaction between the surface hydroxide group and the $M(OH)^+$ species.

Table 1 helps to illustrate the dependence of adsorption of trace metals on pH. The experimentation yielding these results was carried out in two phases. The first phase was designed to load the trace metals onto the manganese dioxide coating from solution. The second step was the system pH lowered systematically by 0.5 units using dilute hydrochloric acid. Although PZC was not reached, desorption had already begun to occur with cadmium, lead and nickel.

Further experimentation on variation in pH was done. The first of these experiments was designed to examine the difference obtained in adsorption in three solutions of pH 5, 6, and 7. Each beaker was spiked with all seven trace

metals and 5 mls of 0.01 N potassium acid phthalate buffer.

The ionic strength of the solution was kept constant by adding calcium chloride to a concentration of 0.1 M. The data derived from

this set of experiments was unable to be used because of an inability to maintain distinct pH levels. Records show that at the end of the test, equilibration of the solution pH values had occurred. The first beaker had a pH of 6.34, the second 4.55, and the final one, 6.54. As a result, this experiment was repeated using 10 mls of 1 M potassium acid phthalate buffer. Two of the three solutions were stable, affording interpretation of the data. Initial review of the results did not afford immediate conclusions. However, as Figures

7-8 show, plots of the logarithm of metal concentration versus time demonstrate that variation in pH may affect several of

the metals. It should be noted that the majority of the plots were made and the curves were obtained using the first three to four hours of data since plotting the remaining values yield a curve rather than a straight line. This would seem to indicate that the adsorption occurring in these experiments is a second order reaction.

For the elements cobalt, lead, silver and zinc, Figures 2-5 show that adsorption occurs at a faster rate at a lower pH, and as pH is increased, the rate decreases. For nickel, the trend is reversed, as is demonstrated in Figure 6. At pH 5 the rate of adsorption is slower than at 6 and 7. Copper shows in Figure 7 a slower rate at pH 5 with pH 6 and 7 having

*Sample was initially spiked with 100 ppb

<u>pH</u>	<u>concentration (ppb)</u>
6.01	114*
7.19	3
6.75	1
6.20	1
5.77	1
5.30	1
4.86	1
4.37	4
3.89	16
3.41	38

metals and 5 mls of 0.01 N potassium acid phthalate buffer. The ionic strength of each was made constant by adding calcium chloride to a concentration of 0.1 M. The data derived from this set of experiments was unable to be used because of an inability to maintain distinct pH levels. Records show that at the end of the test, equilibration of the solution pH values had occurred: the first beaker had a pH of 6.34, the second 6.55, and the final one, 6.54. As a result, this experiment was repeated, using 10 mls of 1 M potassium acid phthalate buffer. The pH of the three solutions was stable, affording interpretation of the data. Initial review of the results did not afford immediate conclusions. However, as Figures 2-8 show, plots of the logarithm of metal concentration versus time demonstrate that variation in pH may affect several of the metals. It should be noted that the majority of the plots were made and the curves were obtained using the first three to four hours of data since plotting the remaining values yield a curve rather than a straight line. This would seem to indicate that the adsorption occurring in these experiments is a second order reaction.

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Figure 2
Variation of pH for Cobalt

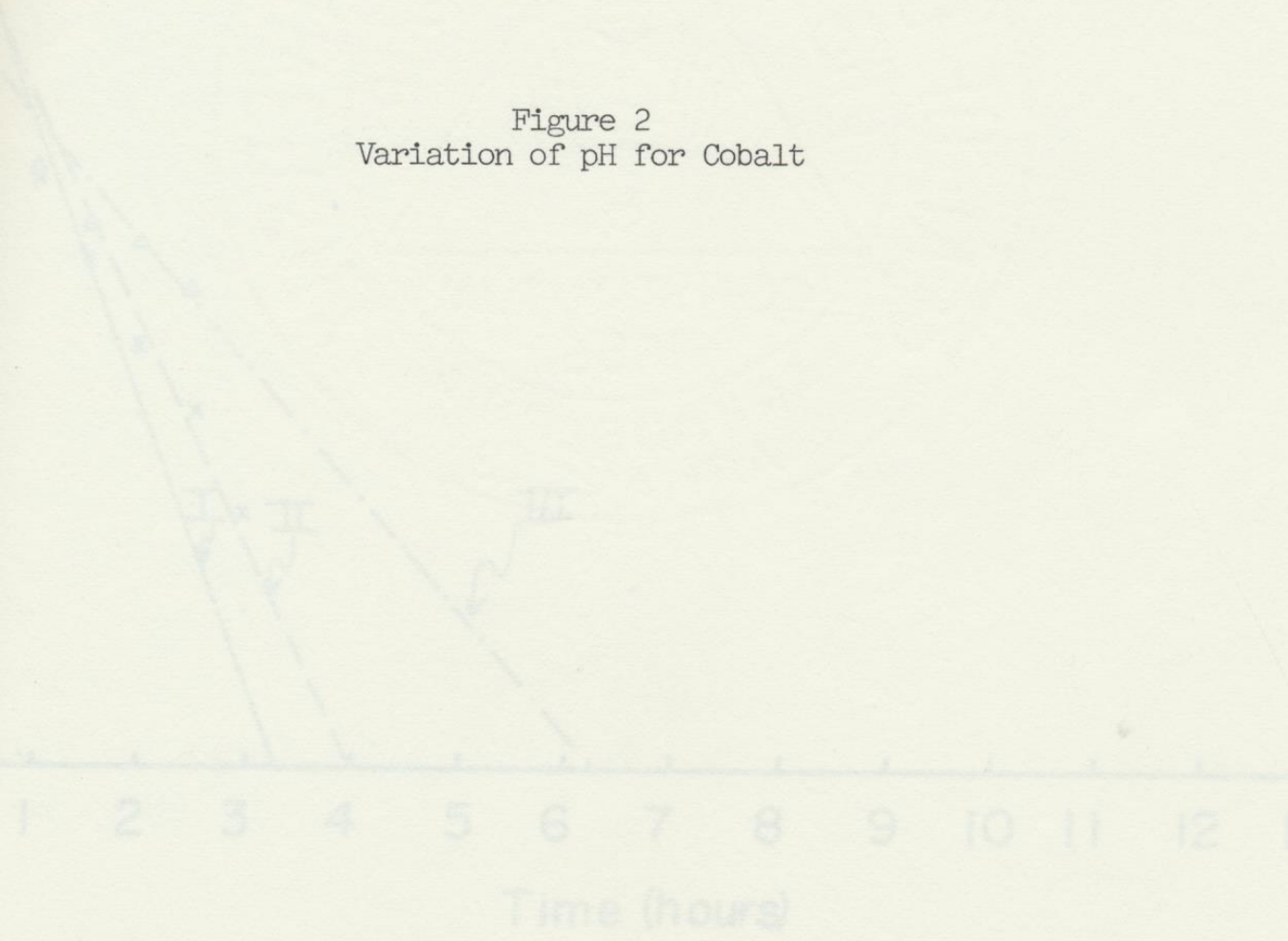


Figure 3
Variation of pH for Lead

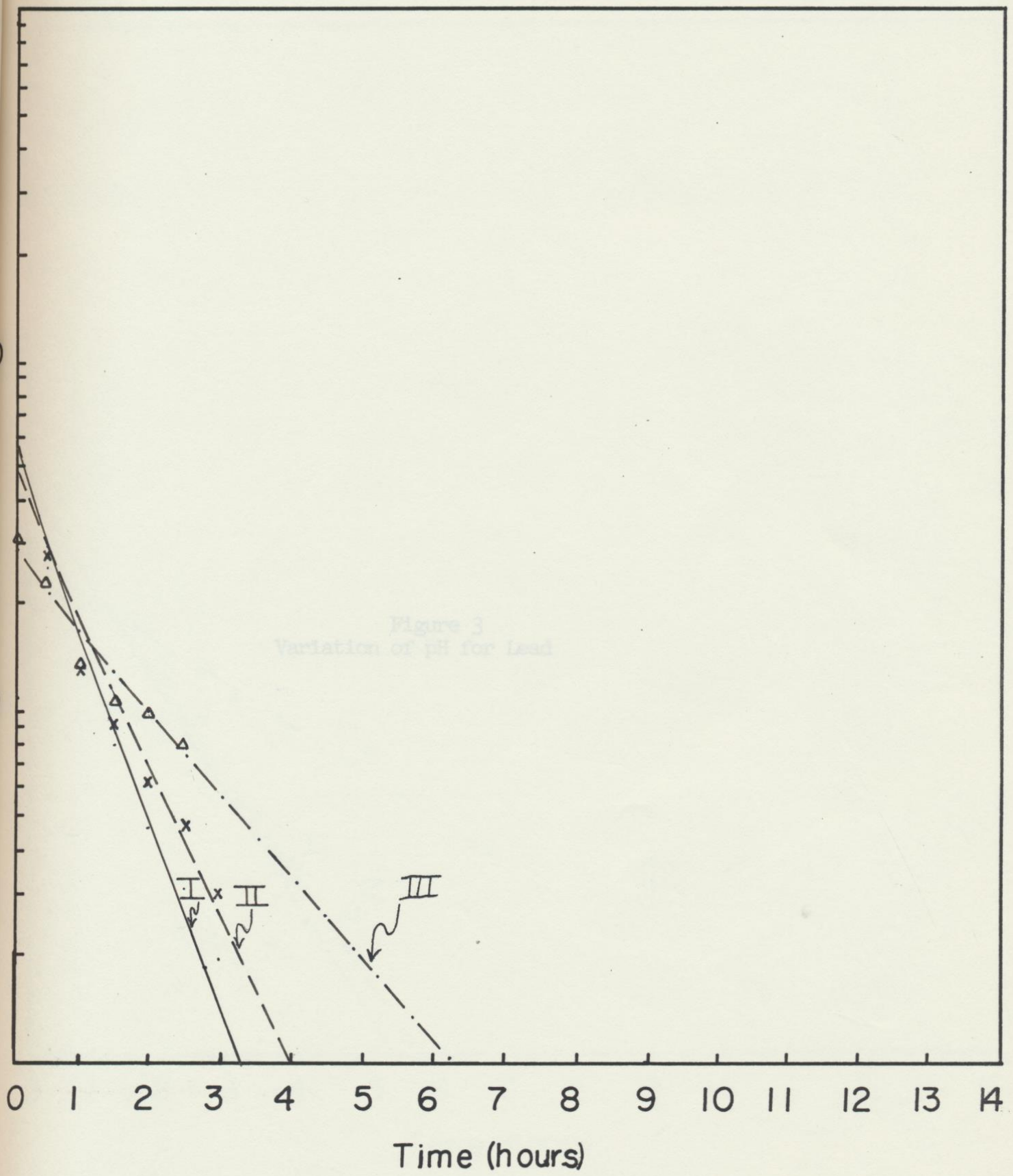
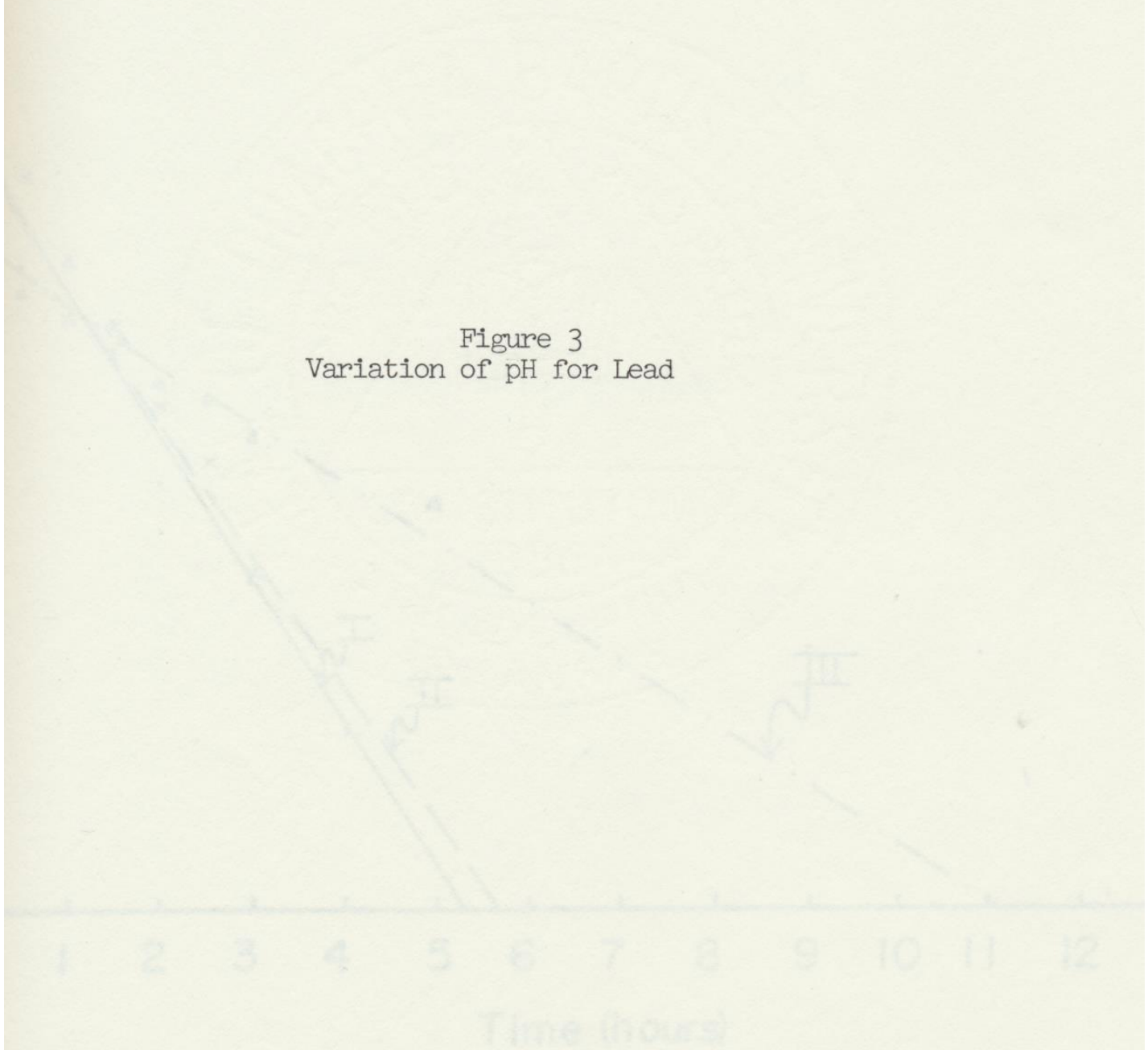


Figure 3
Variation of pH for Lead



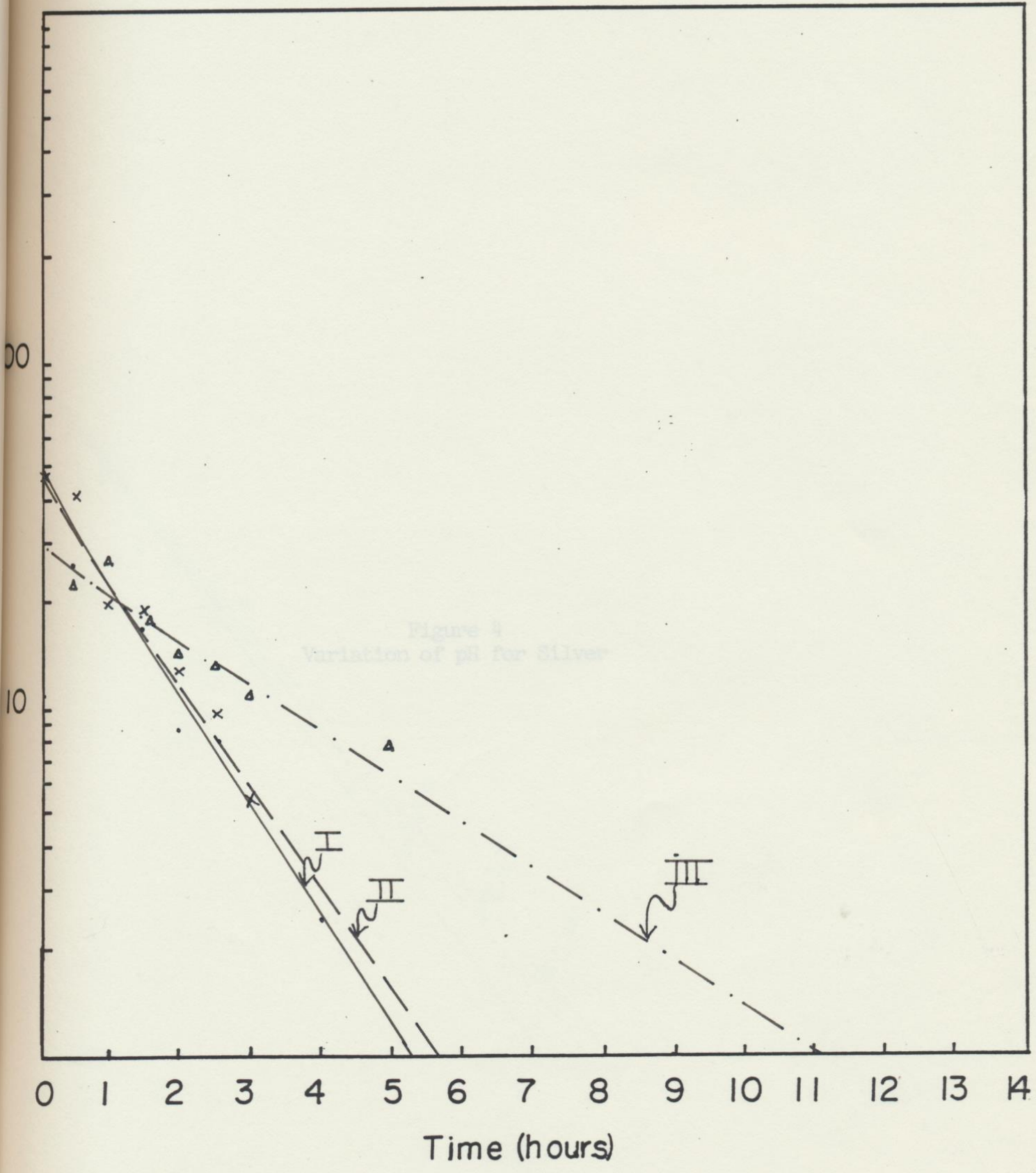
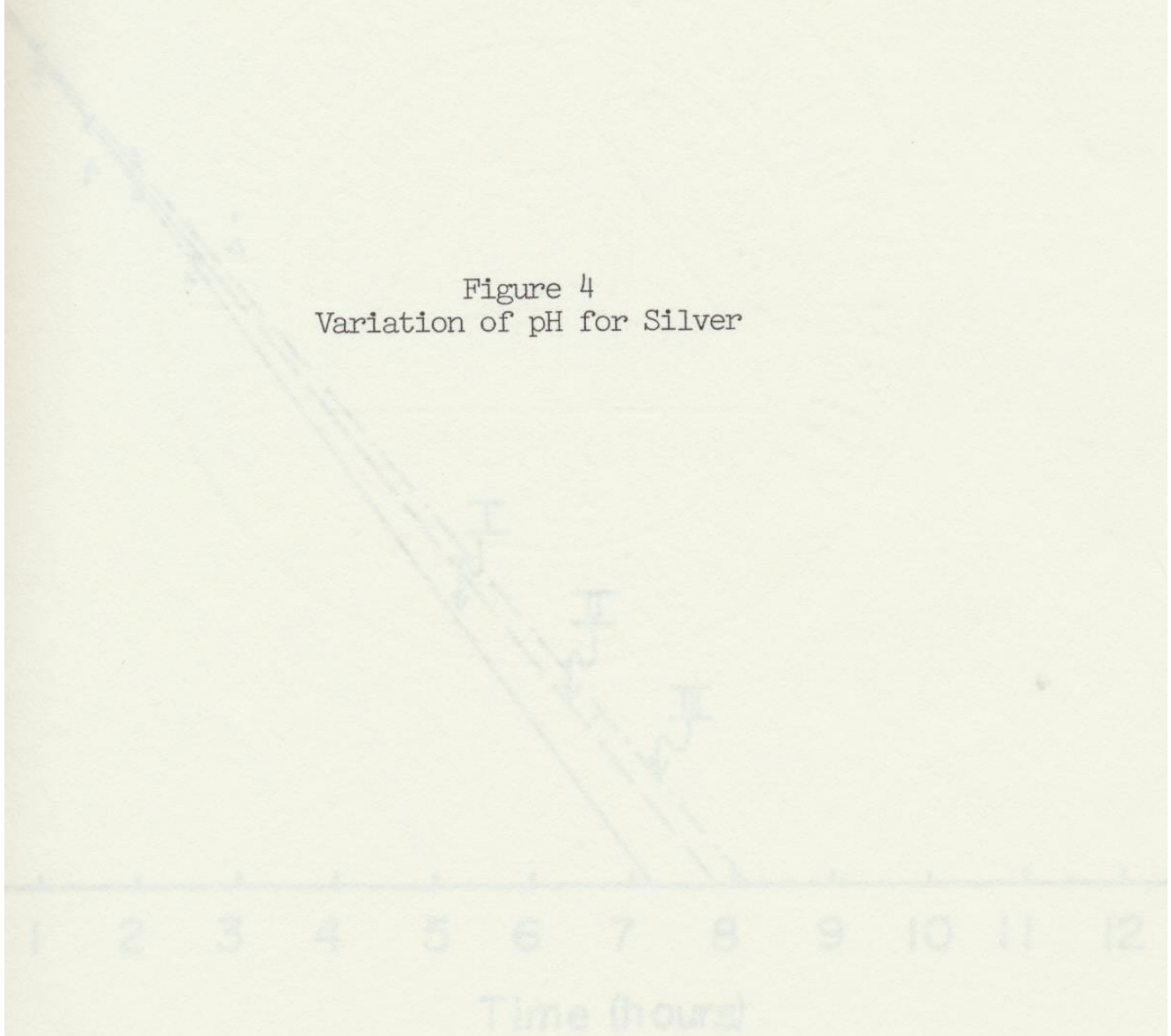


Figure 4
Variation of pH for Silver



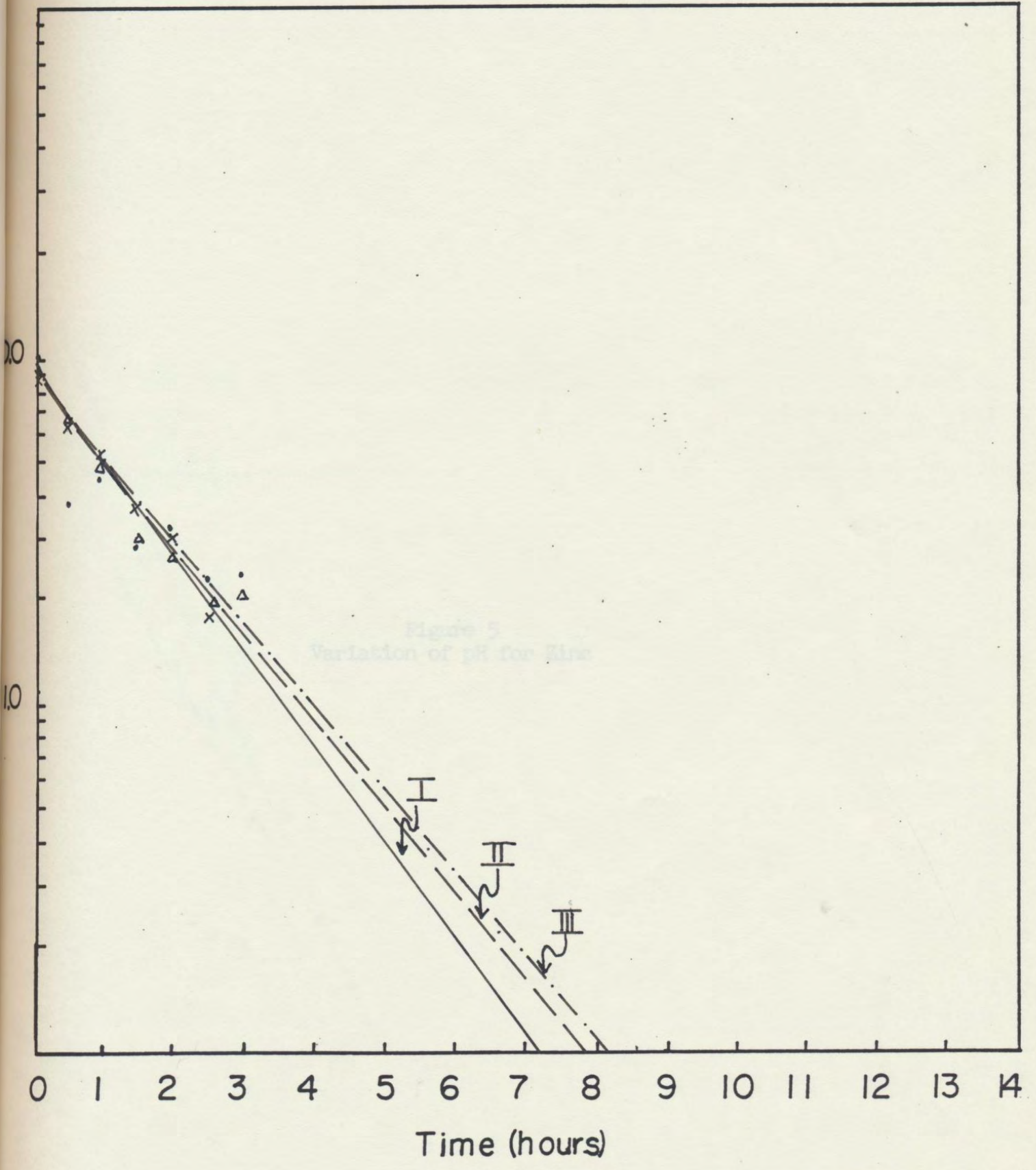
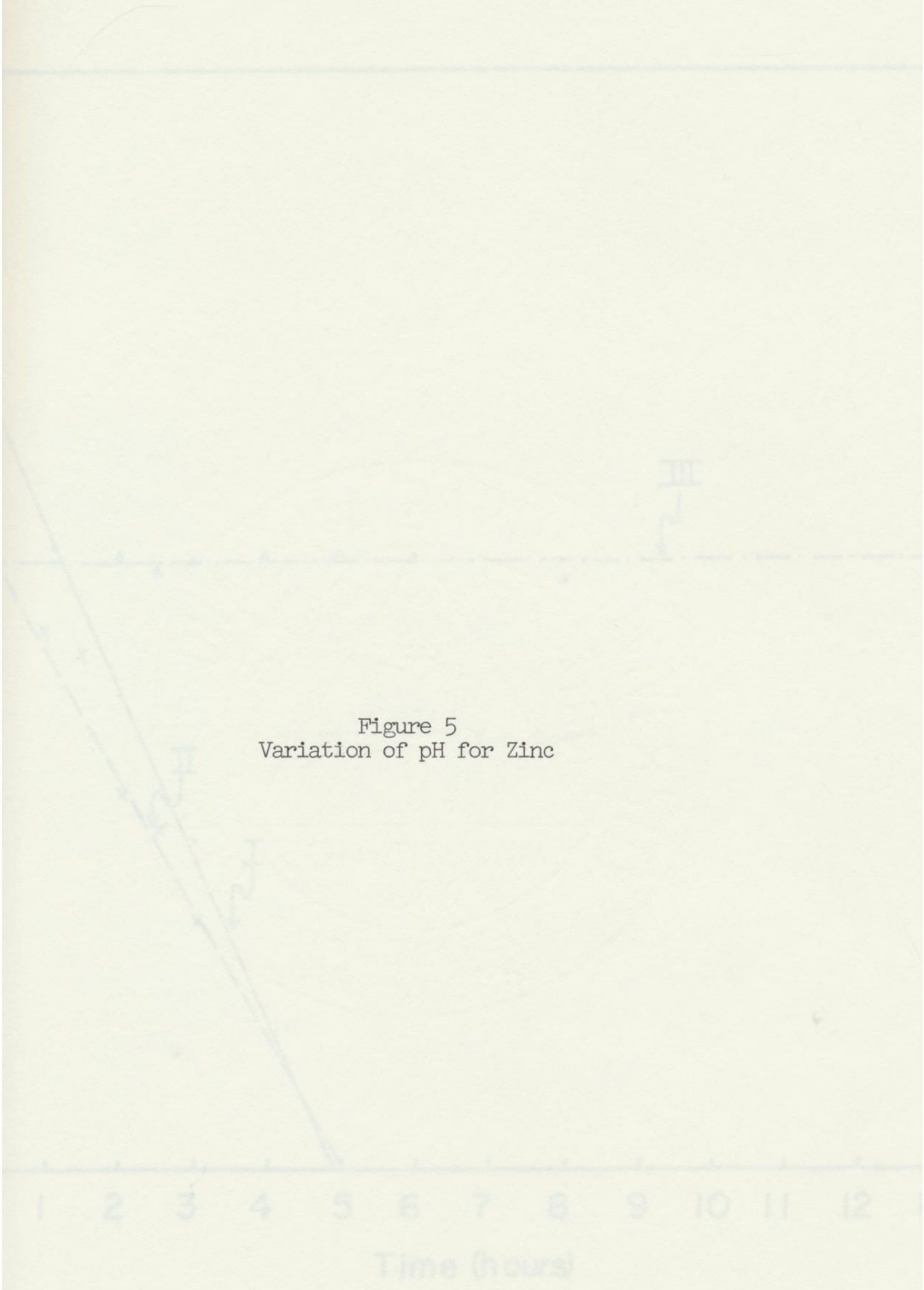


Figure 5
Variation of pH for Zinc



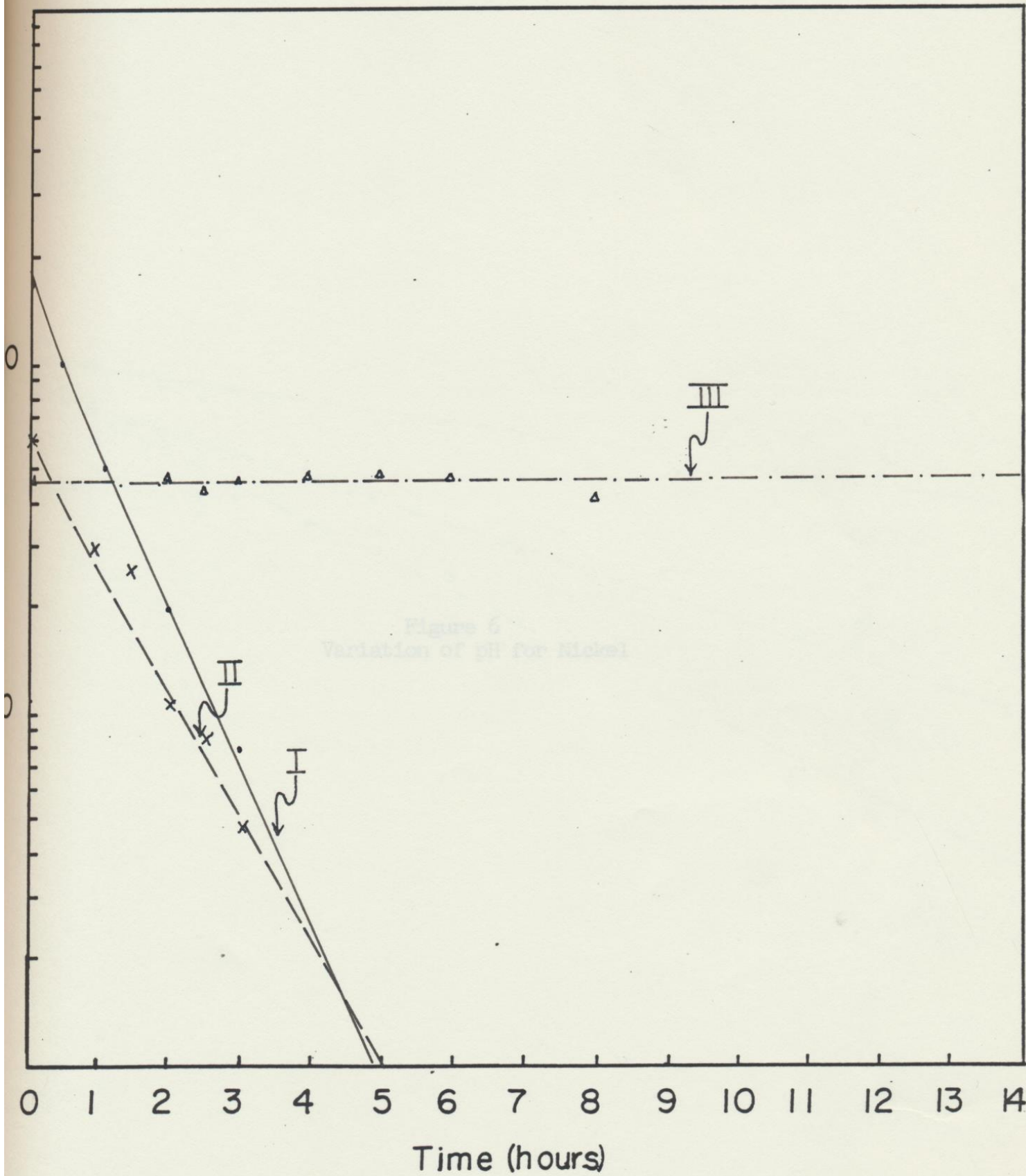
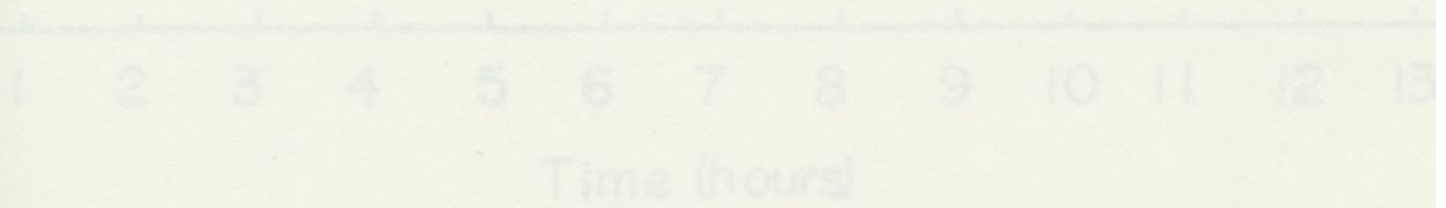


Figure 6
Variation of pH for Nickel



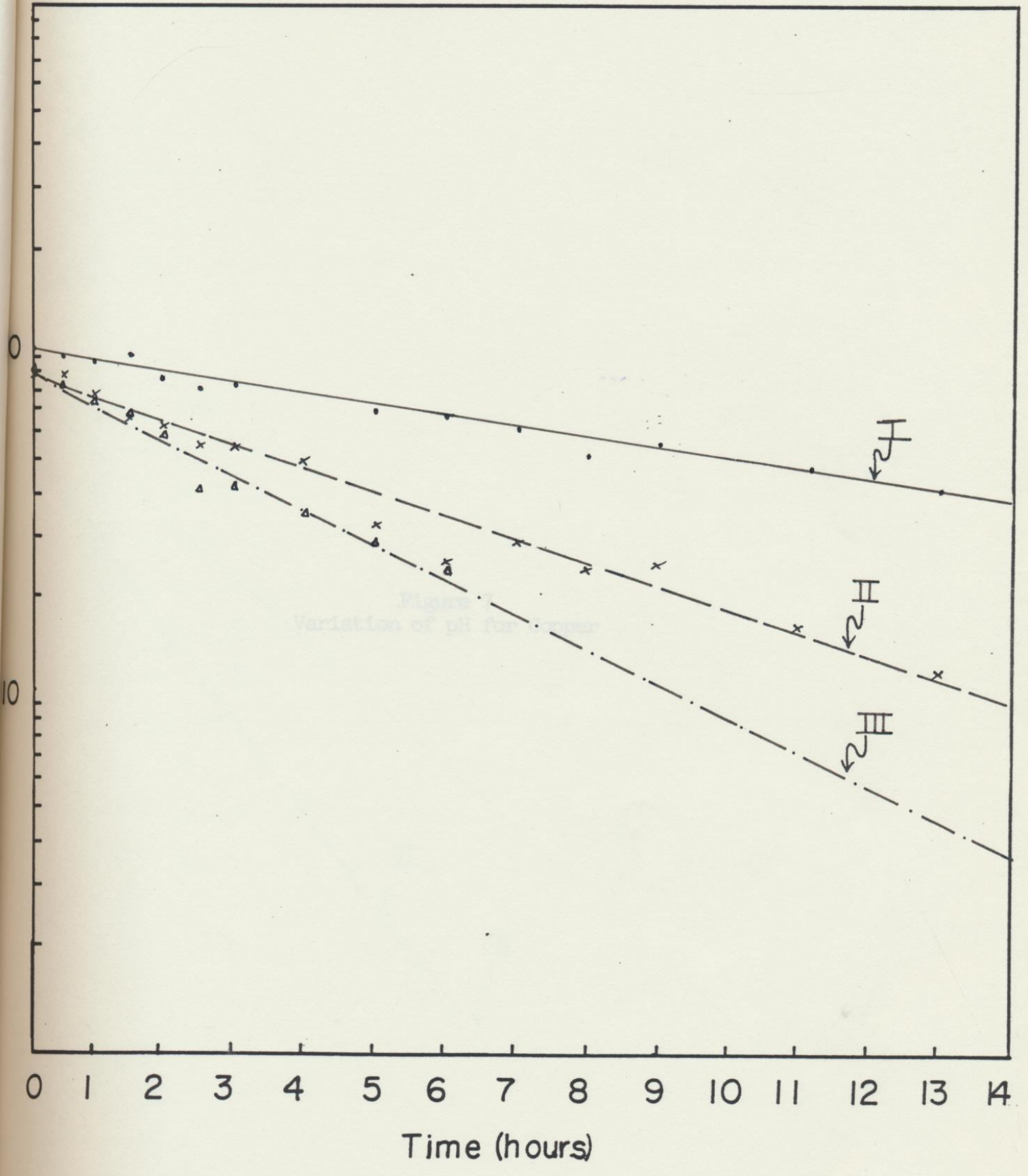
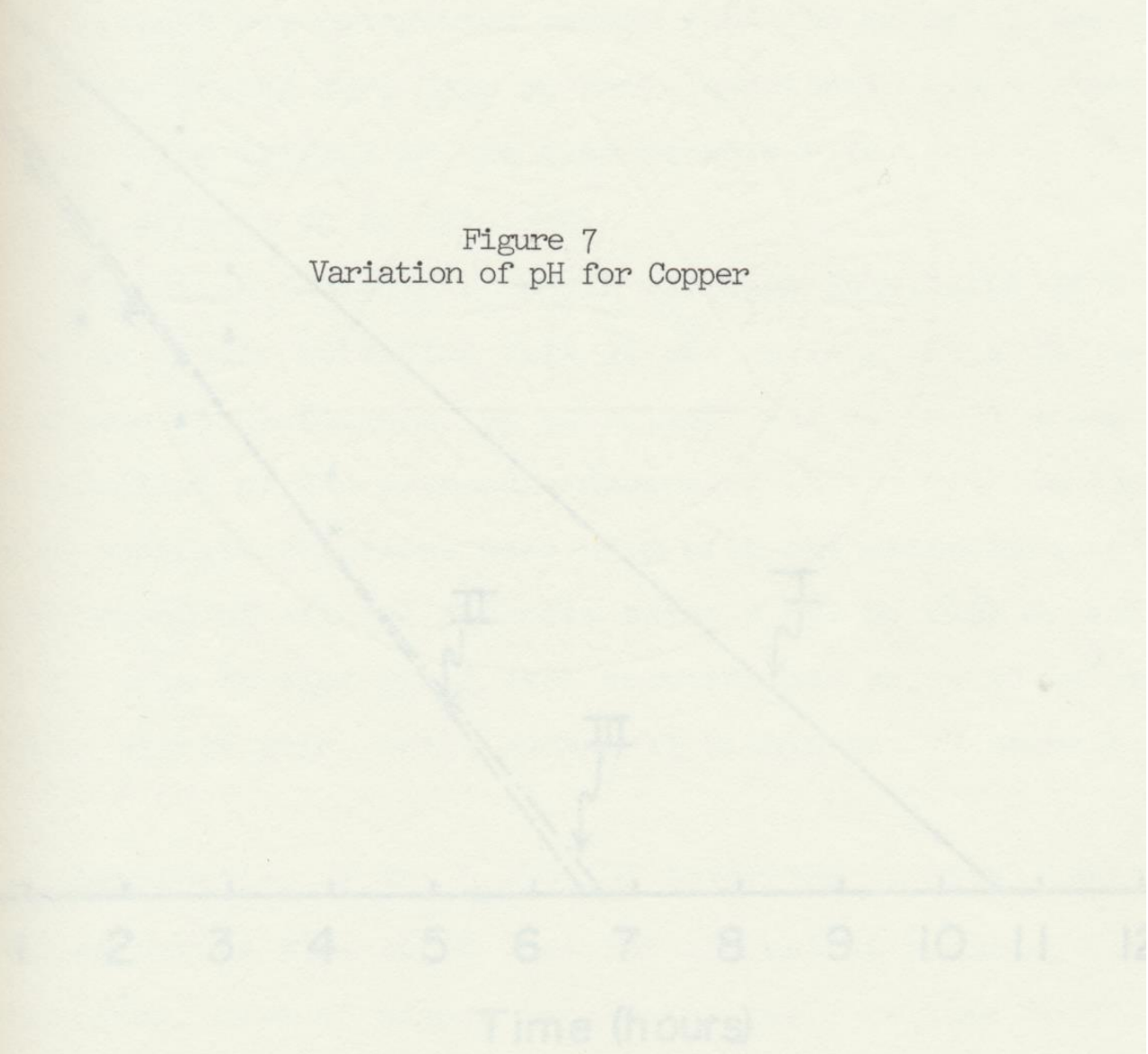
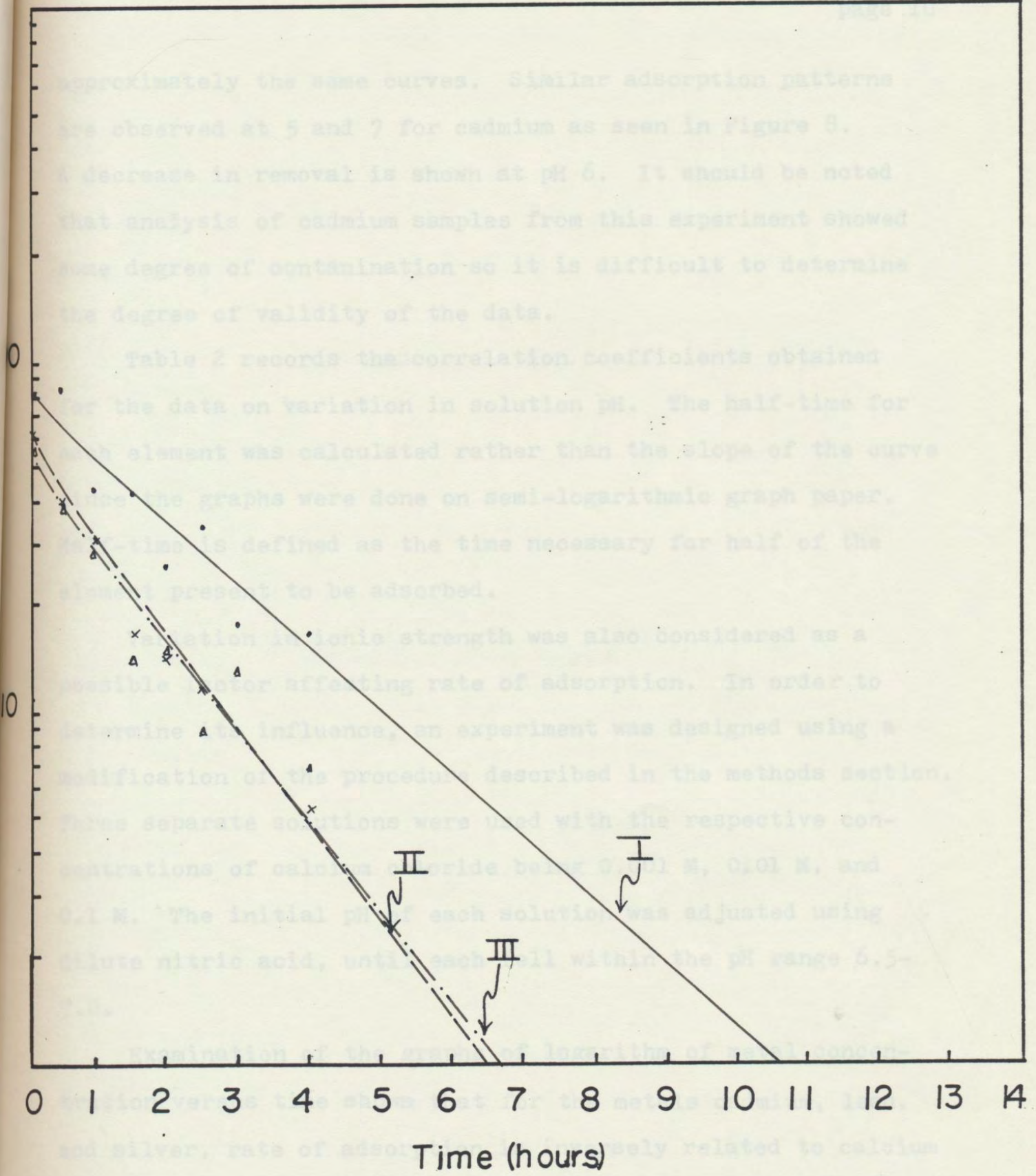


Figure 1
Variation of pH for H_2

Figure 7
Variation of pH for Copper





approximately the same curves. Similar adsorption patterns are observed at 5 and 7 for cadmium as seen in Figure 8. A decrease in removal is shown at pH 6. It should be noted that analysis of cadmium samples from this experiment showed some degree of contamination so it is difficult to determine the degree of validity of the data.

Table 2 records the correlation coefficients obtained for the data on variation in solution pH. The half-time for each element was calculated rather than the slope of the curve since the graphs were done on semi-logarithmic graph paper. The half-time is defined as the time necessary for half of the element present to be adsorbed.

Solution pH and ionic strength was also considered as a possible factor affecting rate of adsorption. In order to determine its influence, an experiment was designed using a modification of the procedure described in the methods section. Three separate solutions were used with the respective concentrations of calcium chloride being 0.1 M, 0.01 M, and 0.001 M. The initial pH of each solution was adjusted using dilute nitric acid, with each fall within the pH range 6.5-7.0.

Evaluation of the effect of logarithm of calcium chloride concentration. Figures 9-11 show that at a concentration of silver, rate of adsorption is directly related to calcium chloride concentration. Figures 9-11 show that at a concentration

approximately the same curves. Similar adsorption patterns are observed at 5 and 7 for cadmium as seen in Figure 8. A decrease in removal is shown at pH 6. It should be noted that analysis of cadmium samples from this experiment showed some degree of contamination so it is difficult to determine the degree of validity of the data.

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Variation in ionic strength was also considered as a possible factor affecting rate of adsorption. In order to determine its influence, an experiment was designed using a modification of the procedure described in the methods section. Three separate solutions were used with the respective concentrations of calcium chloride being 0.001 M, 0.01 M, and 0.1 M. The initial pH of each solution was adjusted using dilute nitric acid, until each fell within the pH range 6.5-7.0.

Examination of the graphs of logarithm of metal concentration versus time shows that for the metals cadmium, lead, and silver, rate of adsorption is inversely related to calcium chloride concentration. Figures 9-11 show that at a concen-

Figure 8
Variation of pH for Cadmium

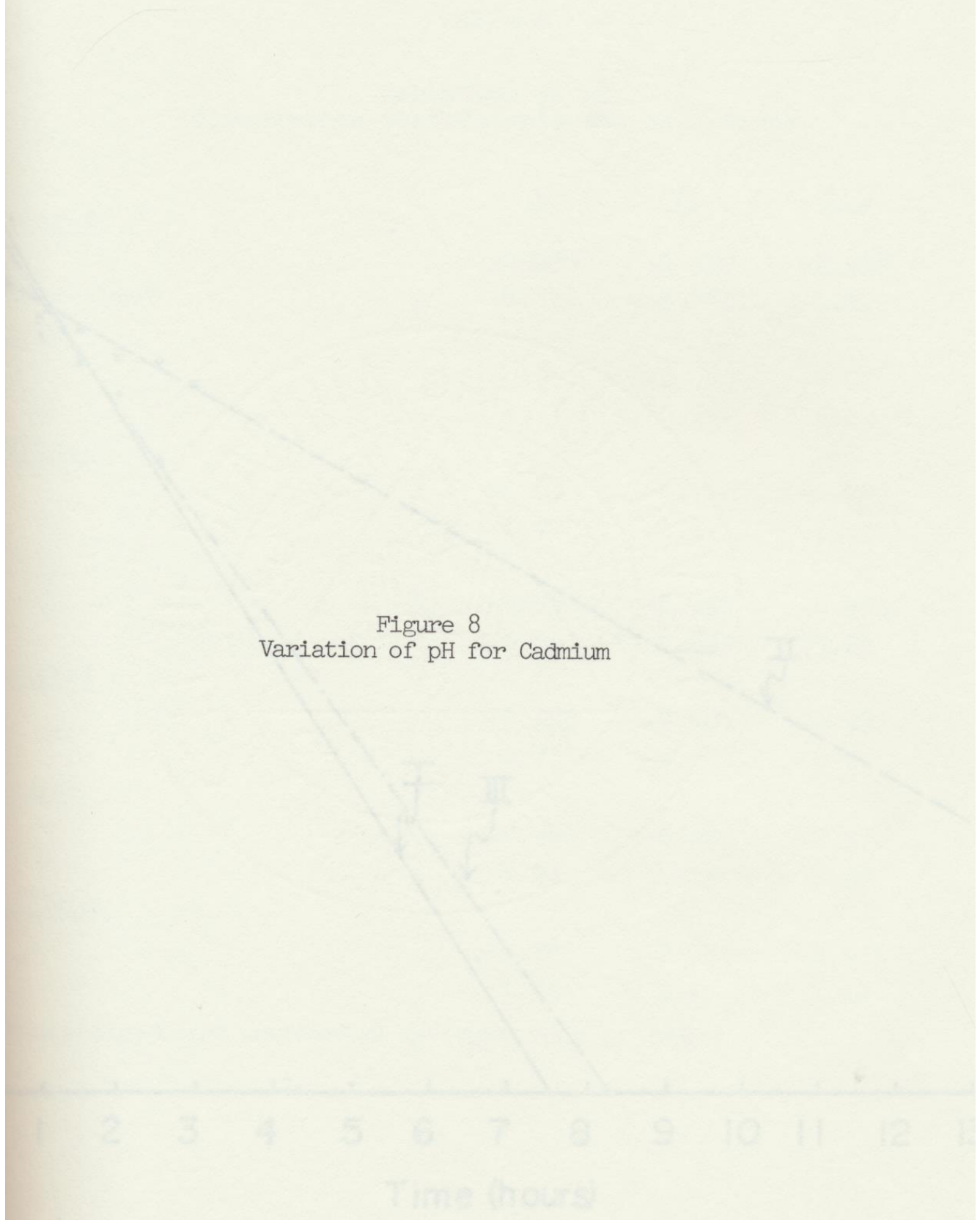
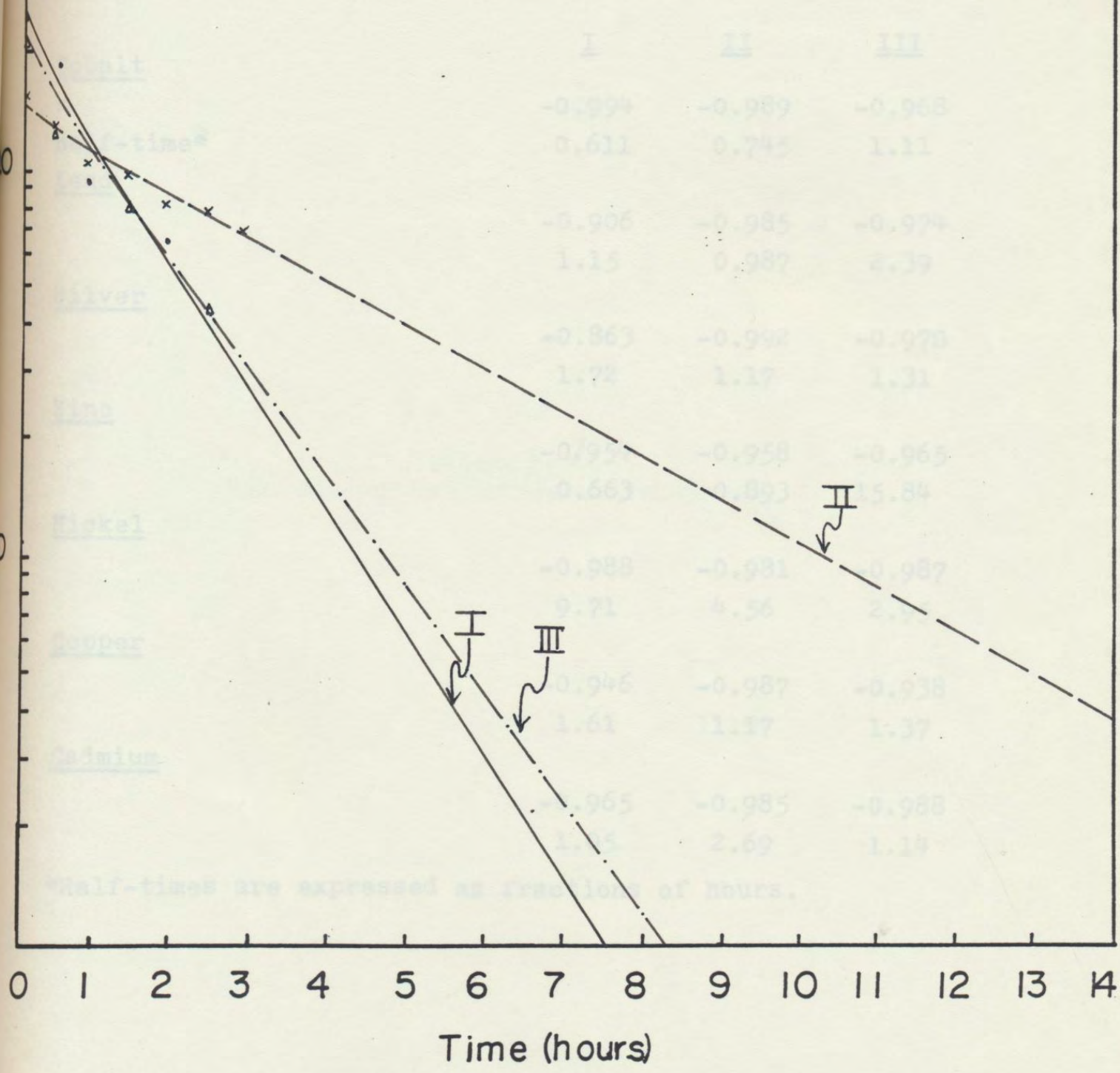


Table 2

Variation of pH
Correlation coefficients and half-times



	I	II	III
Lead	-0.994	-0.989	-0.968
Lead	0.611	0.745	1.11
Silver	-0.906	-0.985	-0.974
Silver	1.15	0.987	4.39
Zinc	-0.863	-0.992	-0.970
Zinc	1.72	1.17	1.31
Nickel	-0.955	-0.958	-0.965
Nickel	0.663	0.893	5.84
Nickel	-0.988	-0.981	-0.987
Nickel	0.71	4.56	2.1
Copper	-0.946	-0.987	-0.938
Copper	1.61	1.17	1.37
Calcium	-0.965	-0.985	-0.988
Calcium	1.75	2.69	1.19

*Half-times are expressed as fractions of hours.

Table 2

Variation of pH
Correlation coefficients and half-times

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	-0.906	-0.985	-0.974
	1.15	0.987	2.39
<u>Silver</u>			
	-0.863	-0.992	-0.970
	1.72	1.17	1.31
<u>Zinc</u>			
	-0.954	-0.958	-0.965
	0.663	0.893	15.84
<u>Nickel</u>			
	-0.988	-0.981	-0.987
	9.71	4.56	2.95
<u>Copper</u>			
	-0.946	-0.987	-0.938
	1.61	11.17	1.37
<u>Cadmium</u>			
	-0.965	-0.985	-0.988
	1.05	2.69	1.14

*Half-times are expressed as fractions of hours.

Figure 9
Variation of ionic strength for Cadmium

1 2 3 4 5 6 7 8 9 10 11 12
Time (hours)

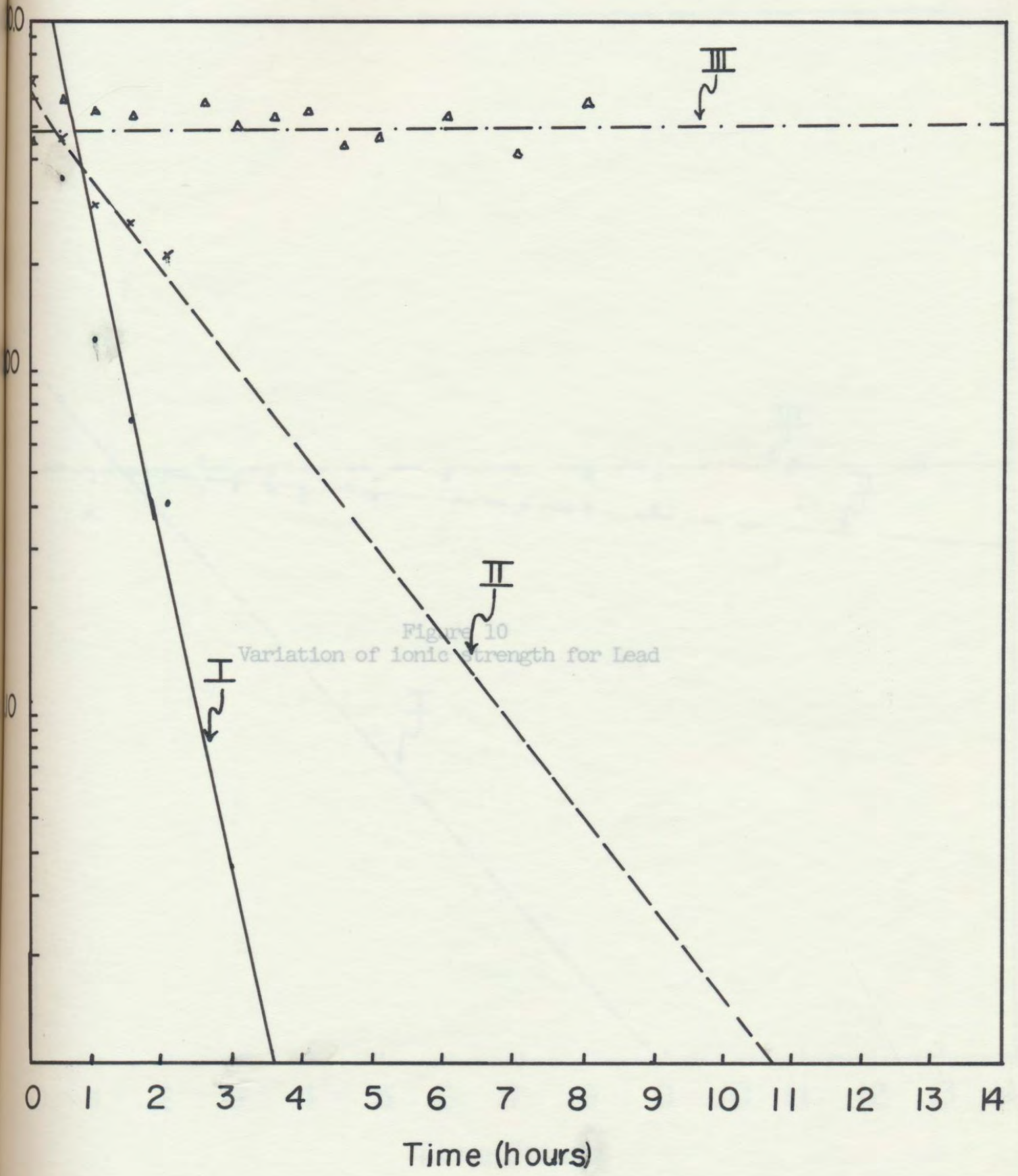
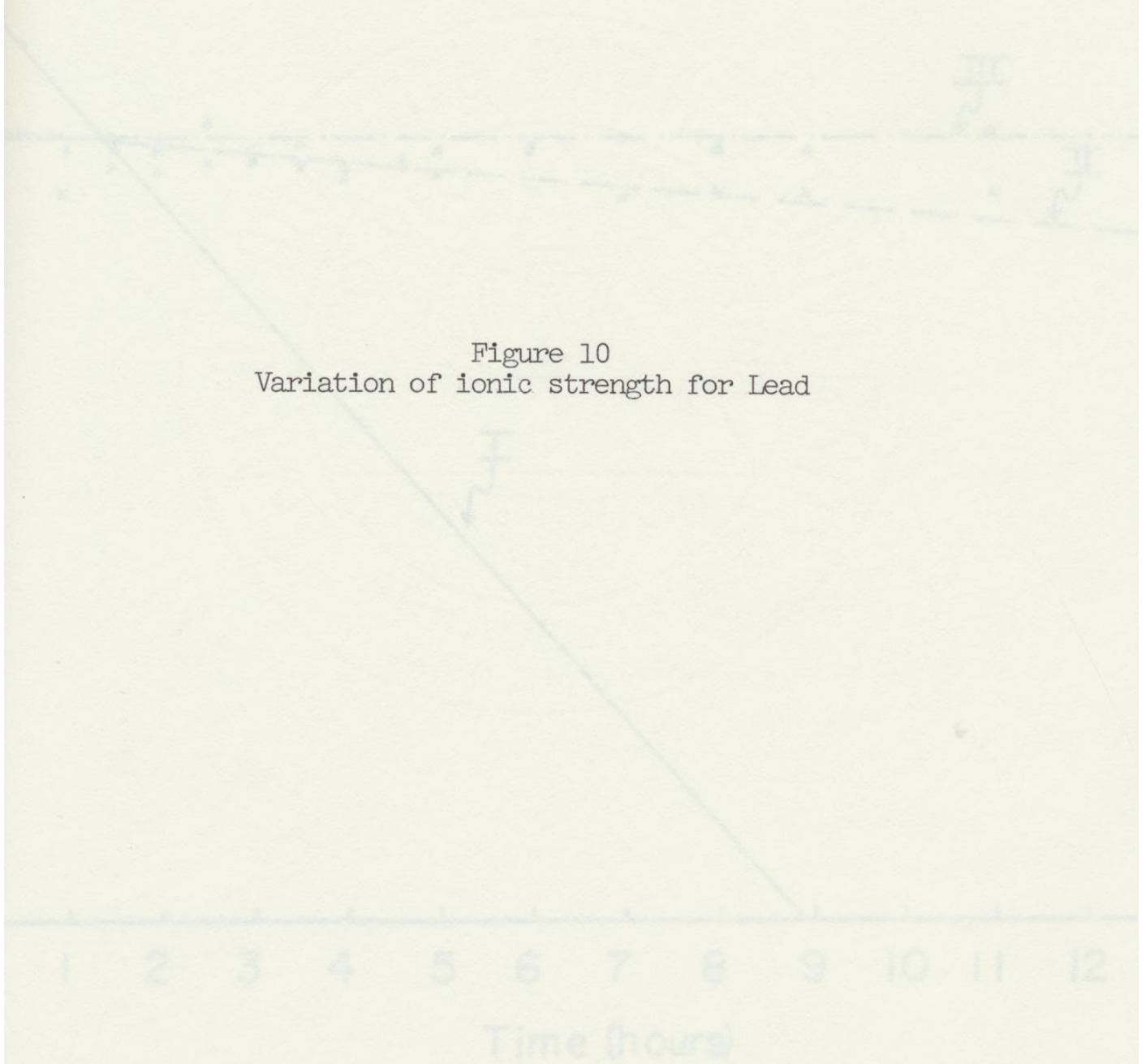


Figure 10
Variation of ionic strength for Lead

Figure 10
Variation of ionic strength for Lead



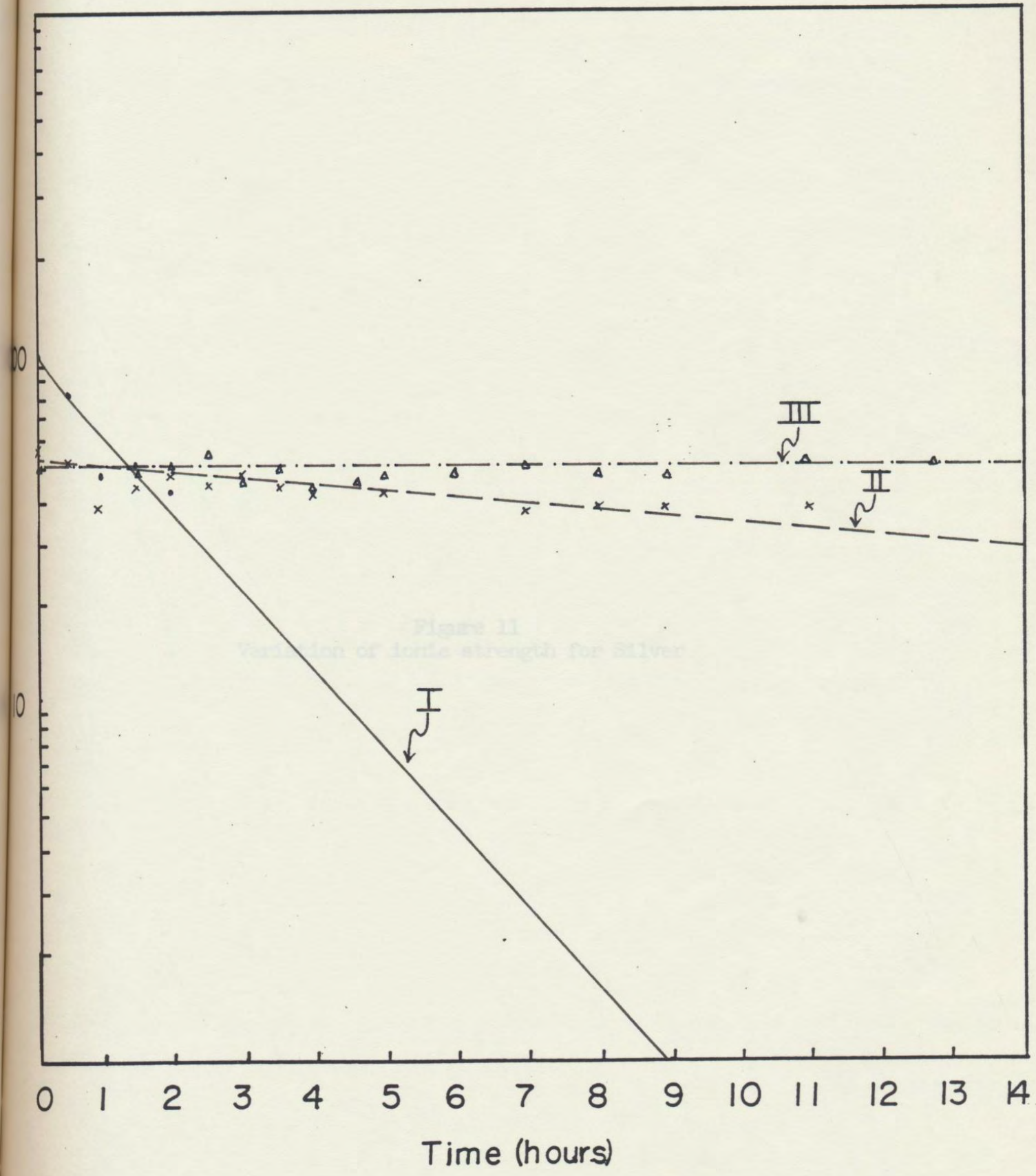
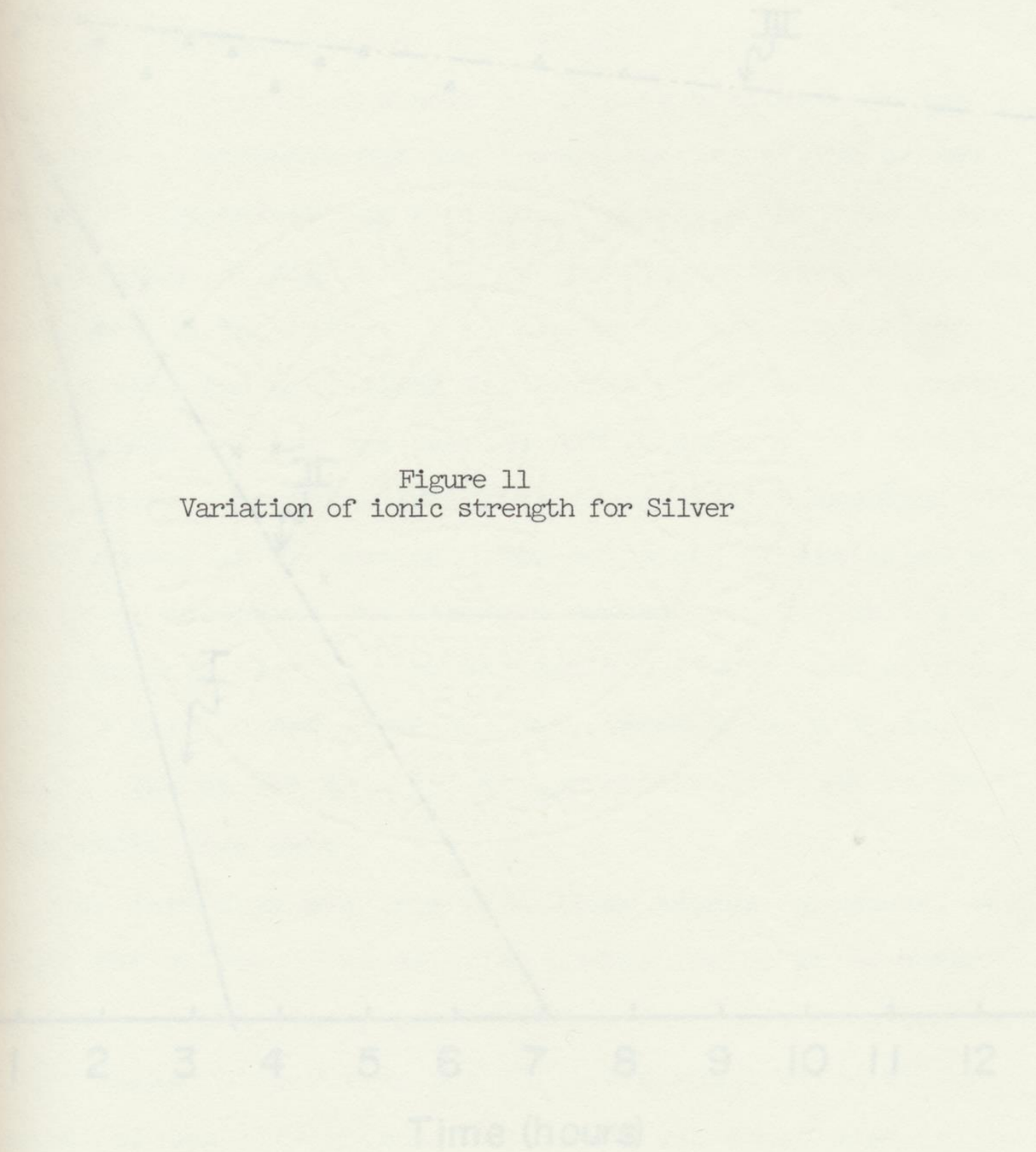
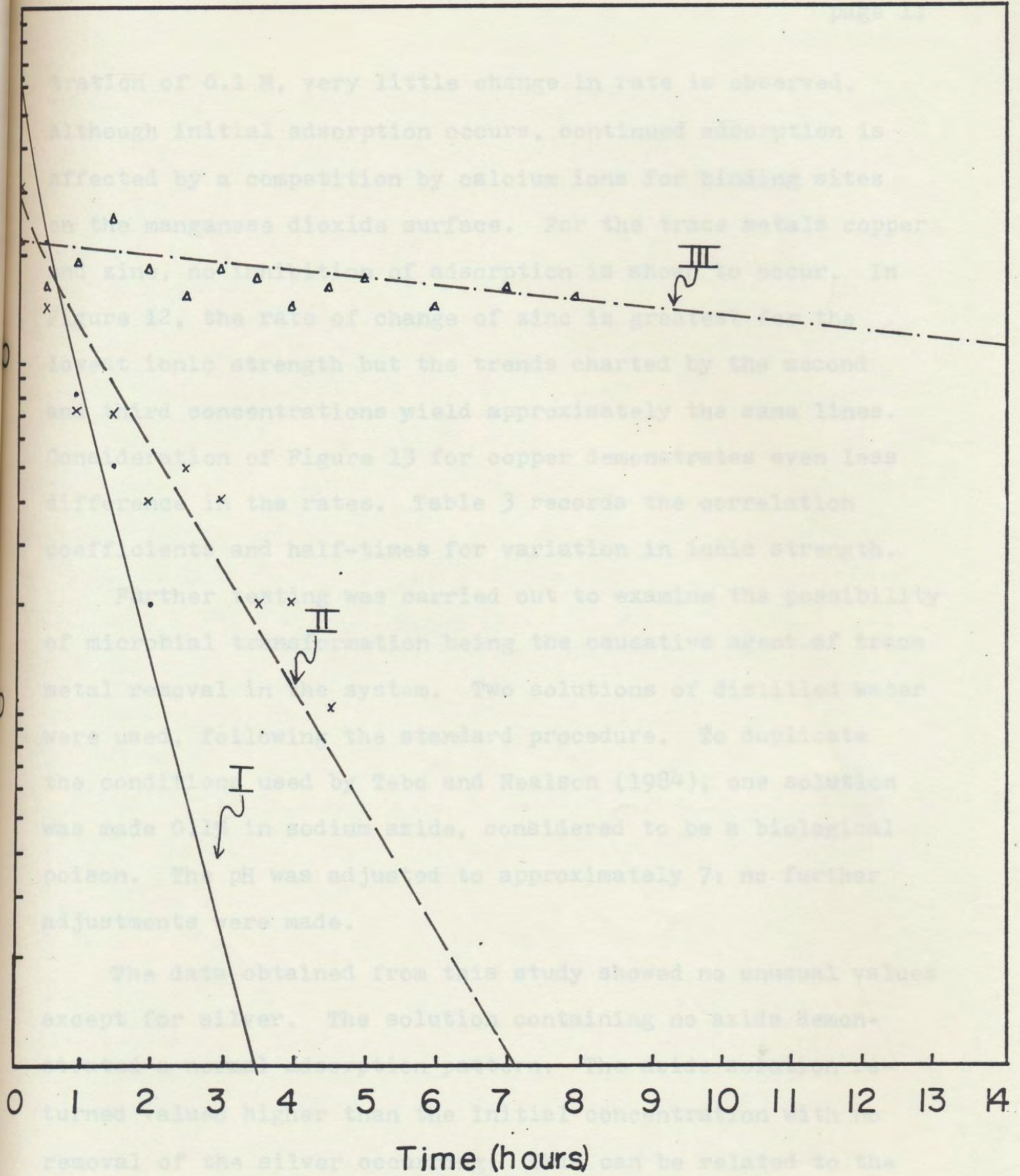


Figure 11
Variation of ionic strength for Silver



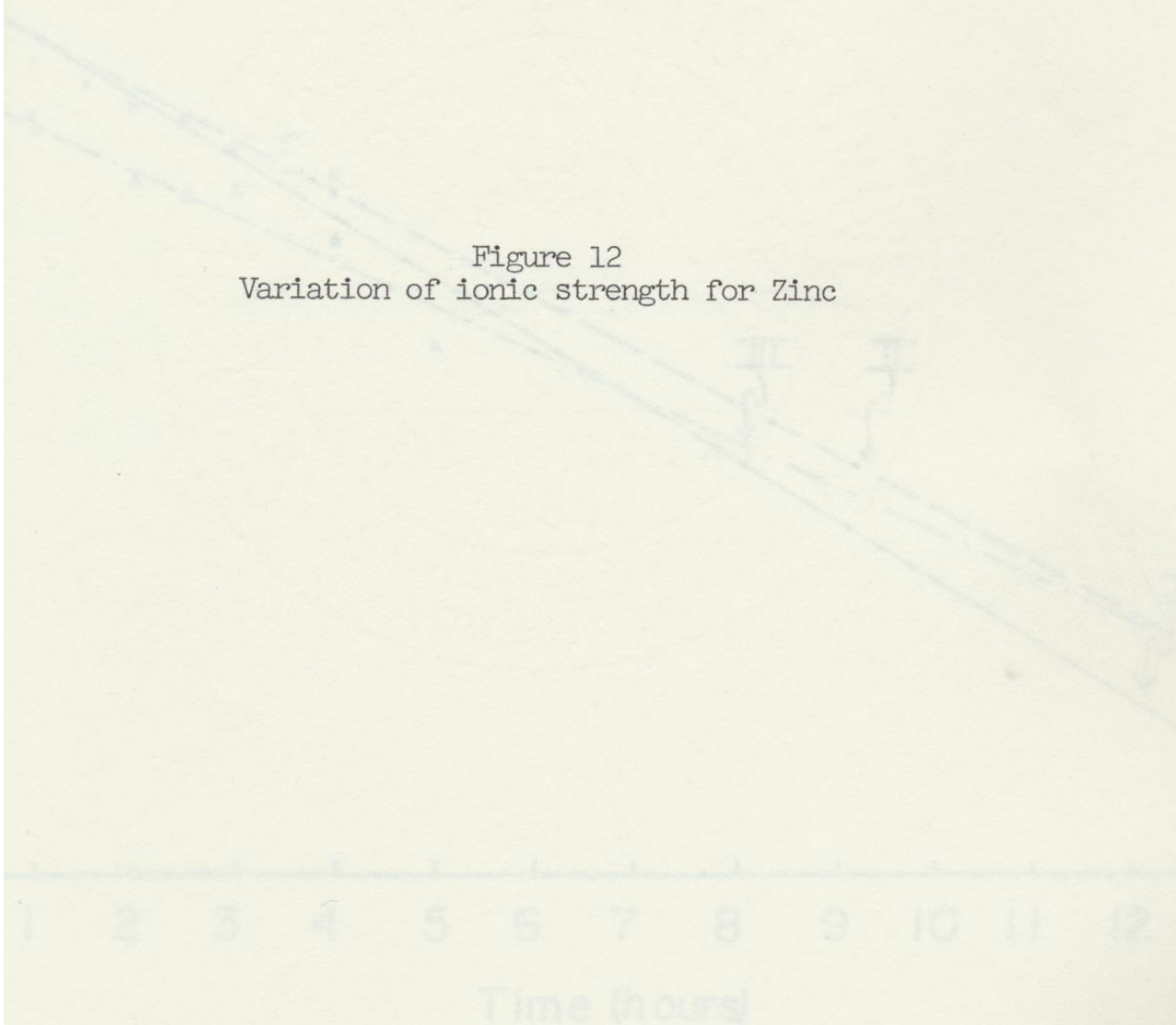


tration of 0.1 M, very little change in rate is observed. Although initial adsorption occurs, continued adsorption is affected by a competition by calcium ions for binding sites on the manganese dioxide surface. For the trace metals copper and zinc, no inhibition of adsorption is shown to occur. In Figure 12, the rate of change of zinc is greatest for the lowest ionic strength but the trends charted by the second and third concentrations yield approximately the same lines. Consideration of Figure 13 for copper demonstrates even less difference in the rates. Table 3 records the correlation coefficients and half-times for variation in ionic strength.

Further testing was carried out to examine the possibility of microbial transformation being the causative agent of trace metal removal in the system. Two solutions of distilled water were used, following the standard procedure. To duplicate the conditions used by Tebo and Nealson (1984), one solution was made 0.1% in sodium azide, considered to be a biological poison. The pH was adjusted to approximately 7; no further adjustments were made.

The data obtained from this study showed no unusual values except for silver. The solution containing no azide demonstrated a normal adsorption pattern. The azide solution returned values higher than the initial concentration with no removal of the silver occurring. This can be related to the formation of solid silver azide.

Figure 12
Variation of ionic strength for Zinc



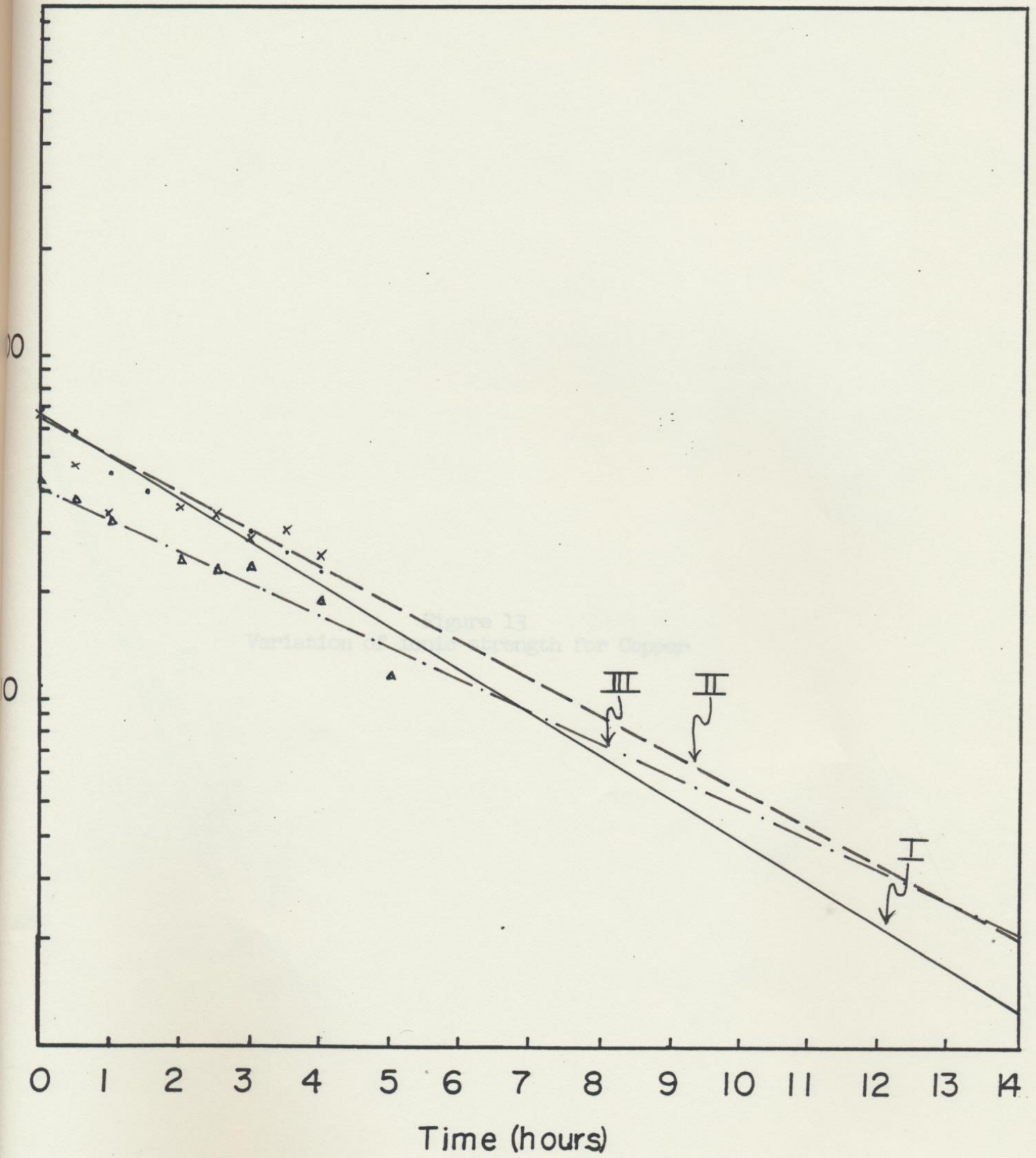


Figure 13
Variation of ionic strength for Copper

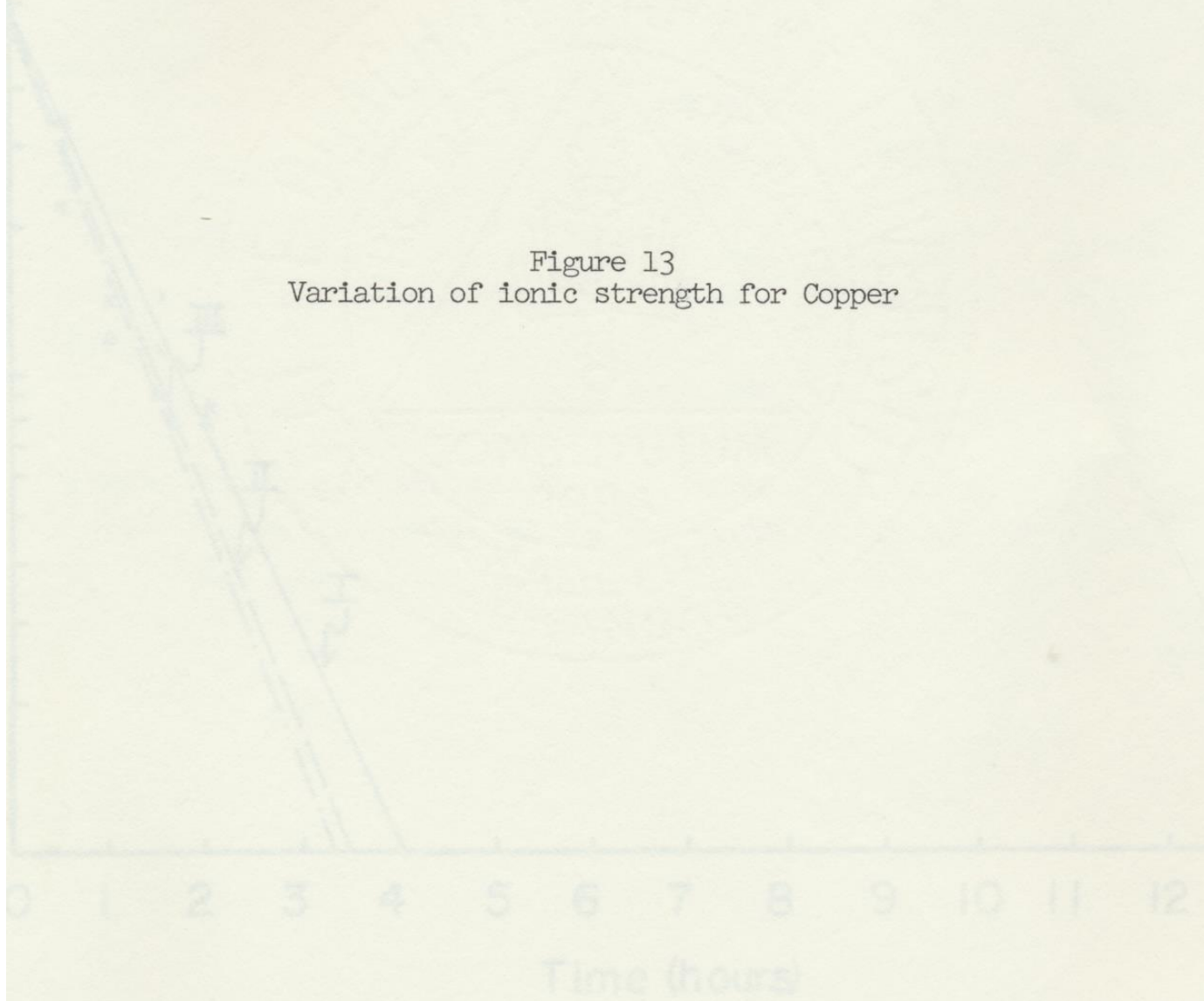


Table 3

Variation of ionic strength
Correlation coefficients and half-times

Cadmium

r	-0.981	-0.974	-0.985
Half-time*	0.410	1.23	----- (See note)

III

r	-0.919	-0.869	-0.970
Half-time*	1.54	0.174	0.176

II

r	-0.993	-0.844	-0.609
Half-time*	0.411	0.736	16.72

I

r	-0.910	-0.888	-0.719
Half-time*	3.27	4.85	4.18

0

r	-0.938	-0.968	-0.952
Half-time*	0.909	0.268	0.675

* Half-times are expressed as fractions of hours

Note: Half-time is given for cadmium III as its slope was calculated as 1.

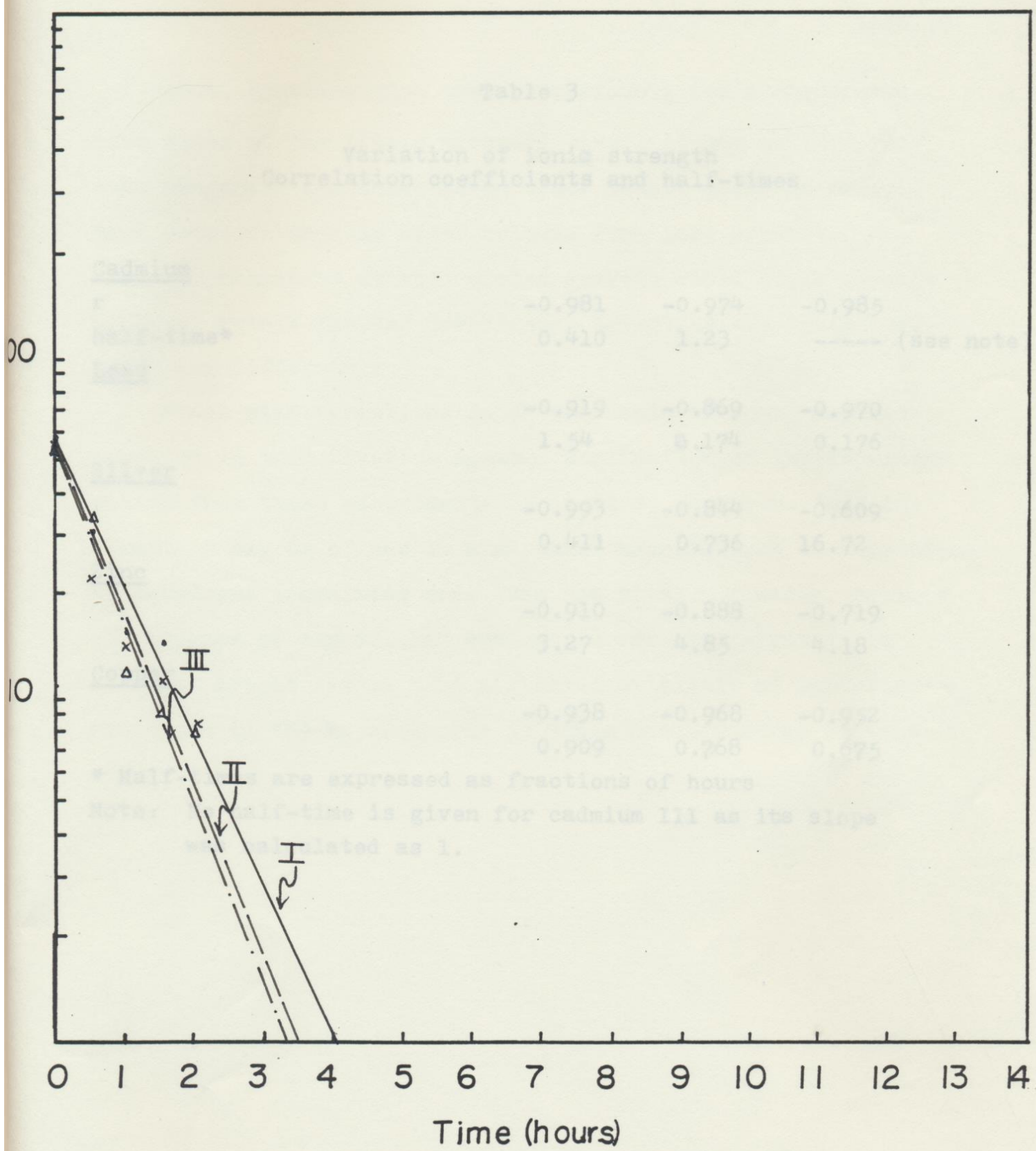


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Lead

r	-0.919	-0.869	-0.970
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Silver

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half-time*	0.411	0.736	16.72

Zinc

r	-0.910	-0.888	-0.719
half-time*	3.27	4.85	4.18

Copper

r	-0.938	-0.968	-0.952
half-time*	0.909	0.768	0.675

* Half-times are expressed as fractions of hours

Note: No half-time is given for cadmium III as its slope was calculated as 1.

Thus, assuming that these experiments are a representative model of the Little Missouri River, it may be inferred that manganese and these seven trace metals would be removed from solution shortly after release from Lake Greeson. Absence of manganese dioxide coated gravels would allow passage of these metals farther downstream, affecting the biological community differently.

Since wide variations in pH and ionic strength are not expected in this riverine system, application of the knowledge gained from these experiments is limited. However, this information may be of use in analytical methods such as separation of solutions containing more than one metal. Finally, because of the lack of significant changes in adsorption rates, it does not appear likely that microbial catalysis of oxidation-reduction is the major source of trace metal removal in this study.

Acknowledgments

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